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FACULTY OF **ENGINEERING AND ARCHITECTURE**

One- and Two-Pot Synthesis of Well-defined Diblock Copolymers by ICAR ATRP: a theoretical exploration

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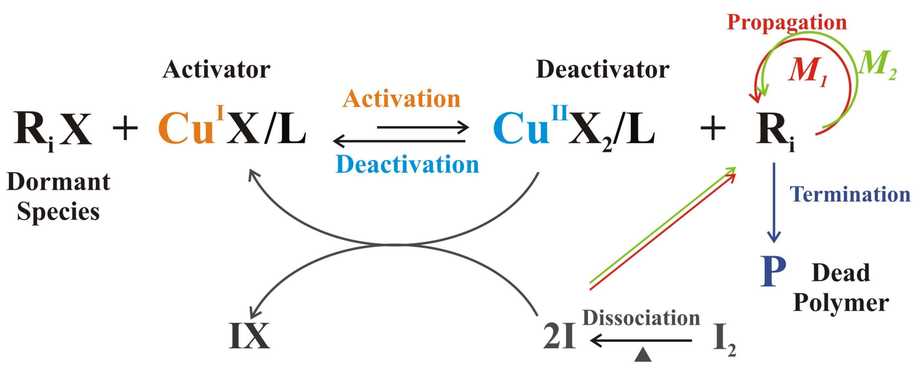
M2dcR2

Initiators for Continuous Activator Regeneration Atom Transfer Radical Polymerization (ICAR ATRP)

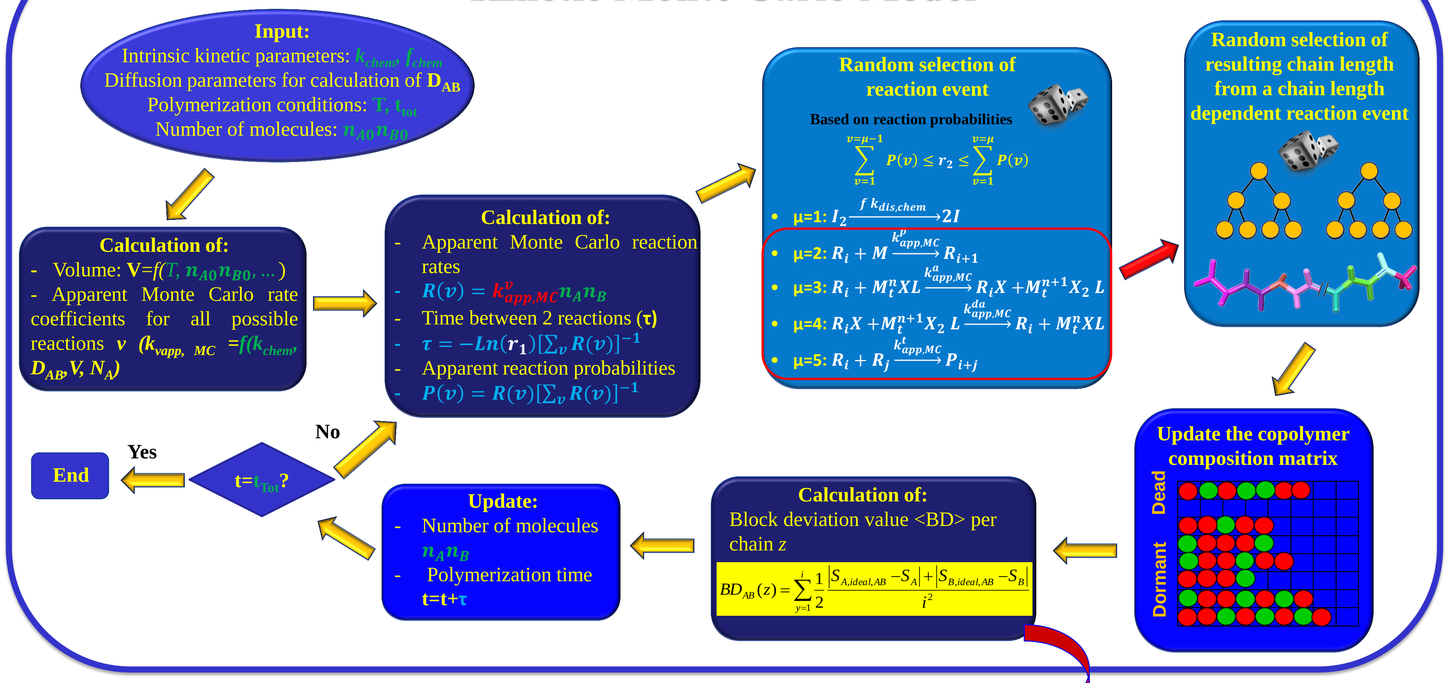
ATRP has been extensively used for the synthesis of diverse macromolecular structures. Although ATRP allows unique polymer properties, the production of large volumes of ATRP based materials is being thwarted by the excessive concentrations of Cu-based catalysts that are usually necessary to achieve a fast and controlled polymerization.[1] The reduction of the catalyst concentration up to 50 ppm has been enable by the introduction of modified ATRP techniques, such as ICAR ATRP in which activator species are regenerated from the deactivator in the presence of a conventional radical initiator, avoiding therefore handling of the air-sensitive activator species and expensive purification operations.[2]



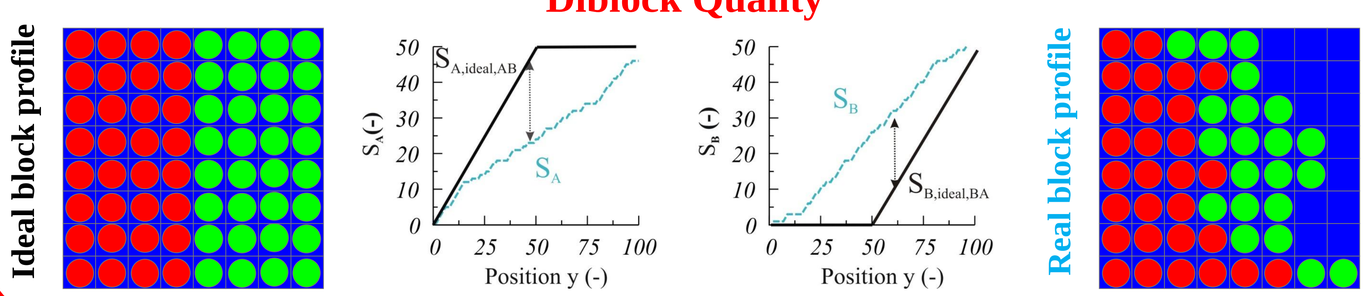
[1] D. F. Grishin et al., *Russian Journal of Applied Chemistry* **2011**, 84, 2021-2028

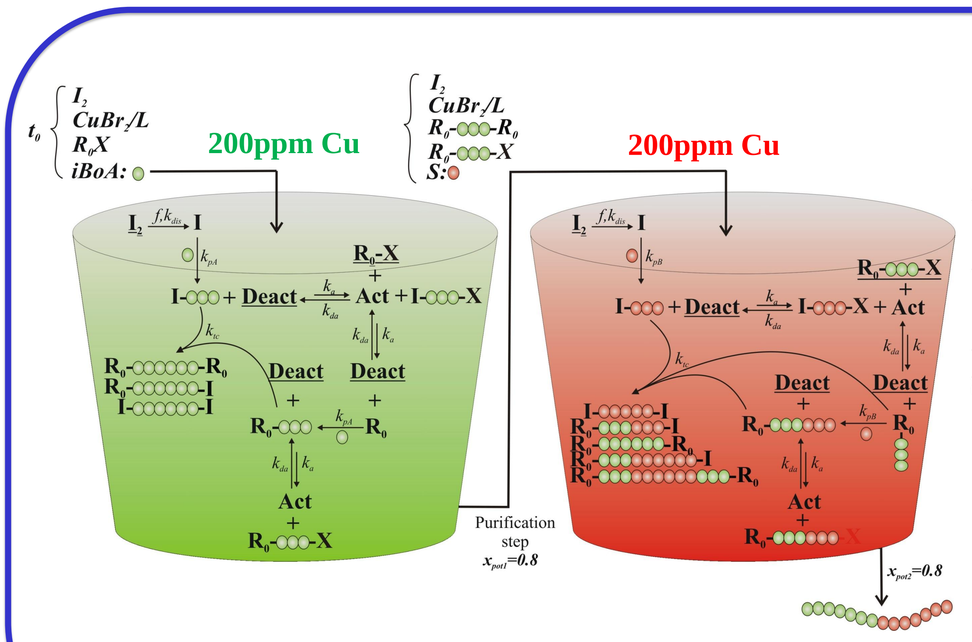
[2] K. Matyjaszewski et al., *Proceedings of the National Academy of Sciences of the United States of America* **2006**, 103, 15309-15314

Kinetic Monte Carlo Model



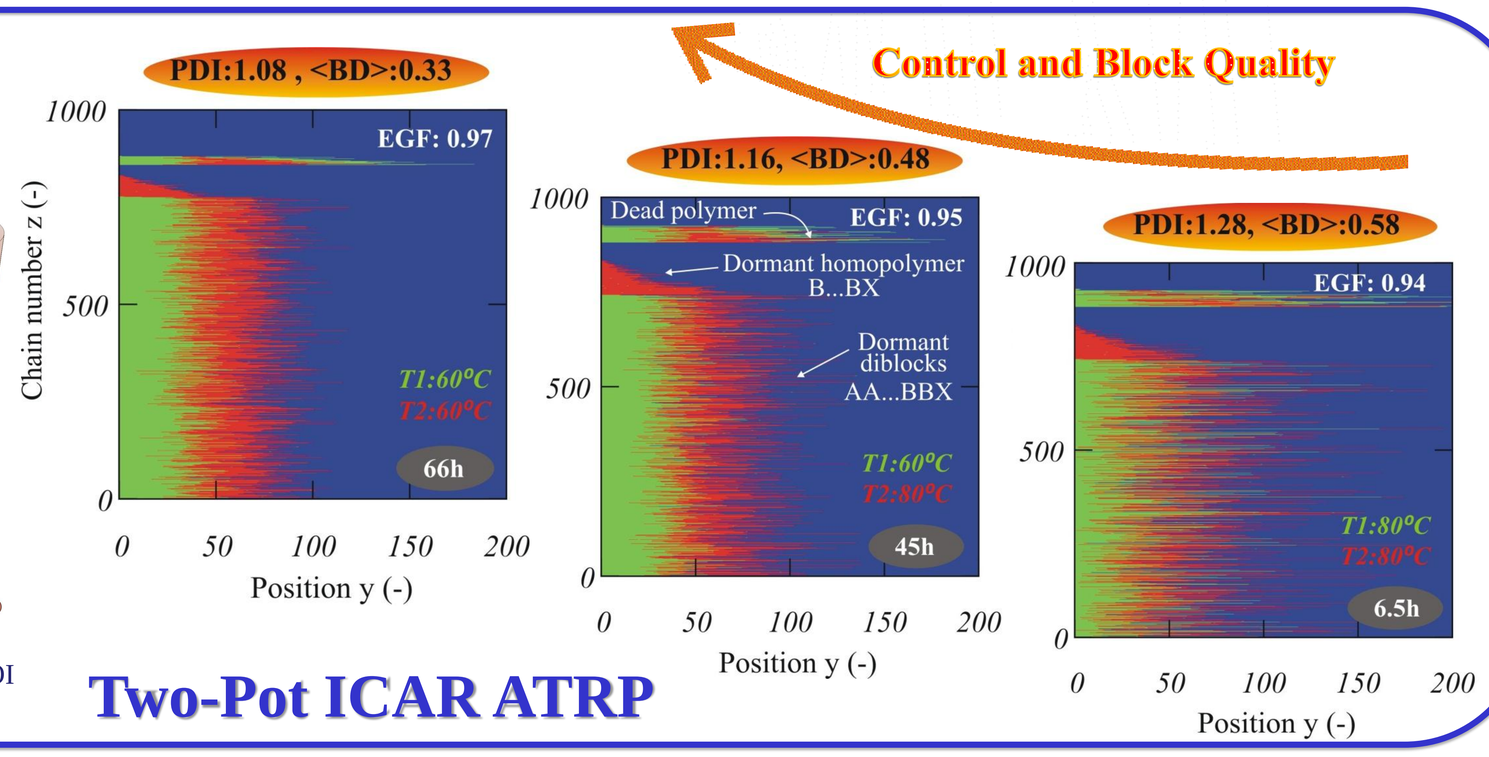
Diblock Quality



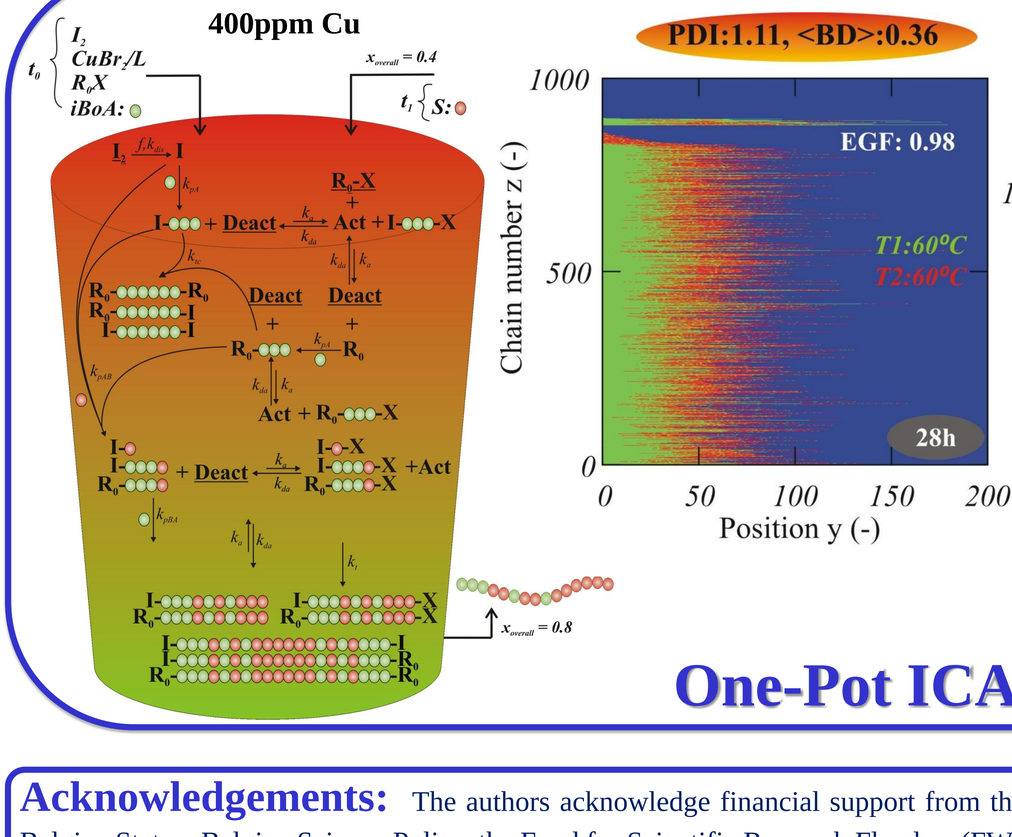


C. Toloza Porras et al., **2013**, *Macromol. React. Eng.*, in press, DOI 10.1002/mren.201200085.

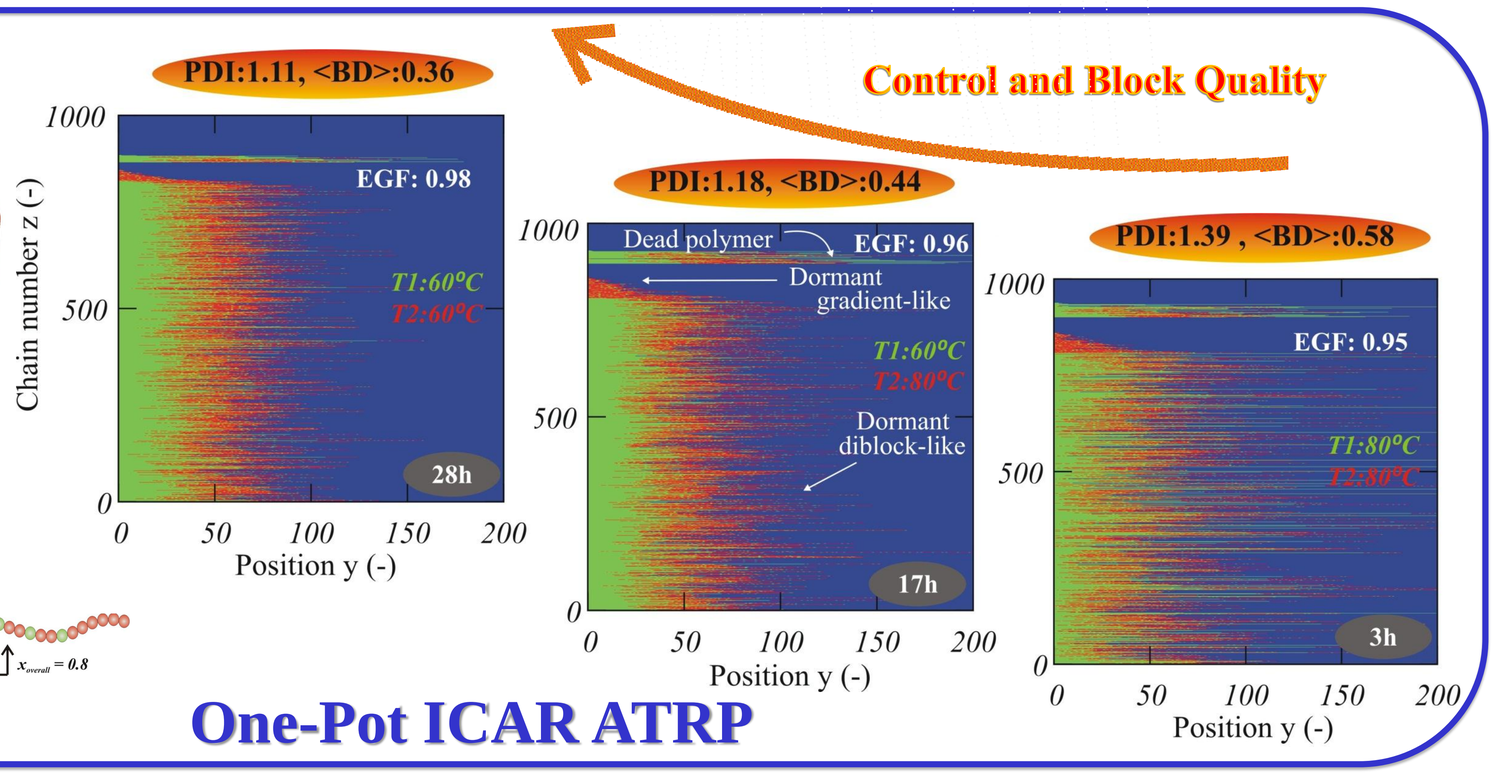
Control and Block Quality



Two-Pot ICAR ATRP



Control and Block Quality



One-Pot ICAR ATRP

Conclusions:

Kinetic Monte Carlo simulations indicate that well-defined poly(iBoA-b-Sty) diblock(-like) copolymers with an average chain length of circa 80 at an overall conversion of 0.80 can be synthesized by bulk ICAR ATRP using both one-pot semi-batch and two-pot batch approaches. In order to quantify the block copolymer quality, a block deviation value (<BD>), which ranges between 0 and 1, is introduced based on the calculation of the explicit copolymer composition. This value reflects the average deviation of a representative polymer sample with respect to perfect diblock reference copolymer chains.

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